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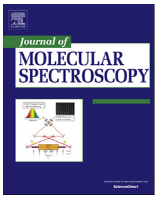

A study of vibrational excitations of ozone in the framework of a polyad preserving model of interacting Morse oscillators

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The vibrational spectroscopic description of the ozone molecule $^{16}O_3$ in its electronic ground state X^1A_1 is presented in the framework of a simple local model, where Morse potentials are associated with both stretching and bending modes. The Hamiltonian is written in terms of internal coordinates considering the local mode character of the ozone molecule. Later on an algebraic representation in terms of Morse ladder operators is introduced through a linear approximation in the expansion of the coordinates and momenta. Three polyads are considered in our study: $P_{11} = v_1 + v_3 + v_2$, $P_{21} = 2(v_1 + v_3) + v_2$, and $P_{32} = 3(v_1 + v_3) + 2v_2$, as suggested by resonances derived from the fundamentals as well as from previous variational analysis. The best description is provided by the P_{11} polyad scheme, yielding an *rms* deviation of 1.85 cm^{-1} for a fit involving 121 energy levels. Considering the other two polyads the description is less accurate: *rms* = 2.78 cm^{-1} for polyad P_{21} and *rms* = 2.63 cm^{-1} for polyad P_{32}, considering 99 and 100 energy levels, respectively. These fits represent the best descriptions in the framework of an algebraic approach. In addition, since our algebraic model keeps the connection with configuration space, the force constants derived from the three fits have been estimated. We have found that all the available experimental energies may be assigned at least to one of the three fits. As the energy increases the eigenstates obtained from different polyad schemes differ. This fact paves the way to establish a polyad breaking approach as a next step to improve the description.

1. Introduction

Ozone is one of the simplest and most studied polyatomic molecule due to its preponderant role in the stratosphere as a protector of living organisms from ultraviolet radiation on the earth, to its importance as a hazardous pollutant in the troposphere as a result of air pollution from internal combustion engines and power plants [1], and to its relevant role in astrophysics to detect the presence of oxygen [2]. Spectroscopy is the natural diagnostic tool to detect and account for the ozone concentration, and hence accurate measurements as well as theoretical descriptions are needed in the IR range [3,4].

Ozone molecule has been the subject of a great variety of studies from both experimental and theoretical point of views. The study of chemical reactions involving dissociation and recombination processes of ozone demands accurate spectroscopic data to validate the potential energy surface (PES) estimated from theoretical models. A study of the PESs of the ground and the lowest excited states with the corresponding fragmentation limits was presented by Banichevich et al., where due to the low dissociation limit the asymmetric $O + O_2$ pathway was considered to be the most likely for fragmentation [5]. Using *ab initio* methods accurate PES for the ground state has been obtained [6–9]. In particular, to provide an accurate vibrational description at energies near dissociation limit, an extended *ab initio* electronic calculations was recently carried out [10].

Rotational analyses of several bands have been done [11–15]. On the other hand, vibrational energies may be calculated using variational methods, where the kinetic energy is calculated in exact form while the potential is expanded in terms of the chosen coordinates, whose associated force constants are determined either through *ab initio* methods or by a fitting procedure to experimental energies. The crucial aspect of these methods relies on the definition of the coordinates and the basis to diagonalize the Hamiltonian. Forty years ago, when the first variational calculations were carried out [16–18], just a few number of experimental energies were available, the quality of the PES was not so good and hence the calculations were not so demanding in accuracy. Nowadays with the new spectroscopic techniques providing high resolution spectra [19–23], theoretical physicists are pushed to offer novel and improved theoretical methods to obtain accurate

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spectroscopic description accordingly to the new experimental data [6–10,24–28].

May be the most simple way to describe a molecular vibrational spectra consists in constructing effective algebraic Hamiltonians based on an expansion of coordinates and momenta in terms of bosonic operators to thereafter fit the spectroscopic parameters [29]. This approach allows the resonances to be identified in a straightforward way. However, being associated with harmonic oscillator bases the use of bosonic operators is expected to induce convergence problems in the high energy region of spectra. In particular low dissociation limits makes unsuitable the models based on harmonic oscillator basis, being the case in the ozone molecule.

A direct consequence of the low dissociation limit of ozone is the implied anharmonicity, which should be manifested as soon as the vibrational excitation increases. Since anharmonicity is connected with locality, a local mode treatment is expected to be more suitable in the description of its vibrational excitations [30–34]. An appropriate description for the stretching degrees of freedom has been proved to be in terms of Morse oscillators, a feature which is reflected both in the basis and the potential expansion variables [35]. On the other hand, the ladder operators for the Morse and Pöchl-Teller potentials [36] satisfy the angular momentum algebra [37]. This connection provides the possibility to obtain an $su(2)$ algebraic representation of a complete vibrational molecular Hamiltonian as long as semi-rigid molecules are considered [38].

The algebraic approach based an $su(2)$ algebras was first constrained to the stretching modes [39–41], but later on it was extended to include additional degrees of freedom of semi-rigid molecules [42–44]. Later on the $su(2)$ approach was reformulated in tensorial form providing a systematic way to construct effective Hamiltonians taking into account in a straightforward way the point symmetry of the system [45]. In any of these formulations the $su(2)$ algebraic models were used in phenomenological way, where the spectroscopic parameters are fitted to the experimental energy levels without any connection with the structure and force constants. In this line the approach provides eigenstates but not potential energy surfaces, being the coherent states approach an alternative to extract the PES [40,44,46,47]. However, in the framework of coherent states the kinetic energy contribution is still missing not allowing predictions of spectra for isotopologue species. This problem was overcome through the explicit connection between the Morse and Pöschl-Teller oscillators with the $su(2)$ algebra [48–50], allowing the PES to be estimated [38], a feature that permitted the description of the Raman spectrum for the carbon dioxide, for instance [51].

The first descriptions of the vibrational excitations of ozone in the $su(2)$ algebraic approach were constrained to the stretching degrees of freedom, all of them considering a rather small number of experimental energies in the fits [39,40,52], a fact that did not permit to evaluate the $su(2)$ model because of its coincidence with the harmonic limit in the low lying of the region of the spectra *Lehmann* [53]. However, as additional experimental energies were incorporated the advantage of the $su(2)$ model became evident. For example, the complete vibrational description given by Pérez-Bernal et al. [54], including a total of 42 experimental energies with an rms deviation of 2.5 cm^{-1} represents a remarkable improvement with respect to the harmonic description, although without connection with configuration space. Since then no new vibrational descriptions including the new available experimental energies using algebraic approaches have been appeared, may be due in part to the highly accurate descriptions using *ab initio* PES. Any phenomenological algebraic description involves a dangerous risk when no further tests for the eigenvectors are carried out: computation of transition intensities for instance. This is manifested in Ref. [54], where it was not found evidence for the need to include the Darling-Dennison interaction, which is in contrast to current calculations.

Ozone has also been analyzed using modern methods of non linear classical mechanics, which has been applied to molecular resonance spectra [55,56]. In particular bifurcation structure has been investigated with a Hamiltonian including Darling-Dennison as well as Fermi interactions [56].

In this contribution we present an algebraic treatment based on three interacting Morse oscillators. In our approach the Hamiltonian is first established in configuration space to be transformed into an algebraic representation through the connection of the $su(2)$ algebra to the Morse oscillator. In this way we keep the connection with coordinates and momenta, allowing the potential force constants to be estimated. An algebraic treatment has the advantage of being able to express the interactions with a precise effect on the polyad manifold. Hence it is possible to deduce Hamiltonians preserving different polyads neglecting from the outset the non-preserving interactions. This is particularly important for ozone, since three different polyads may be used in its description, two of them suggested by resonance criteria and the other one from variational calculations. The aim of this work is to make a detailed study of the vibrational spectrum of ozone taking account the whole set of available experimental energies. Our approach does not intend to compete with *ab initio* methods, but rather offer a simple algebraic local approach based on $su(2)$ algebras to obtain a reasonable spectroscopic description keeping the physical insight involved in the PES and eigenfunctions.

This paper is organized as follows. In Section 2 the Hamiltonian in configuration space is established in accordance with the interactions belonging to the different polyads. Section 3 is devoted to obtain the algebraic representation of the Hamiltonian. In Section 4 the basis used to assign local and normal mode characters is presented. Section 5 is dedicated to present the spectroscopic analysis for the fits associated with the three polyads, together with the estimation of the corresponding force constants. Finally, our summary and conclusions are given in Section 6. Supplementary material including the explicit form of the Hamiltonian in configuration space, the spectroscopic parameters as a function of the force constants and predicted energy levels is also given.

2. Hamiltonian in configuration space

The aim of this section is to establish the Hamiltonian to describe the vibrational excitations of ozone in configuration space. To this end we start identifying the possible relevant polyads to thereafter set up the corresponding Hamiltonians. Our approach is based on the expansion of the kinetic energy in terms of internal coordinates [35], in contrast to variational methods based on considering its exact contribution.

The equilibrium geometry of ozone is non linear with structure parameters $r_e = 1.2727$ Å, and $\angle OOO = 116.75^\circ$ [8]. In our description we shall neglect the tunneling between minima and employ the molecular symmetry group $C_{2v}(M)$ [57]. In this way we also disregard the metastable ring equilateral triangle structure [58]. This molecule has three degrees of freedom, three of them associated with the $A \oplus B$ stretching modes plus the A bending mode. The harmonic approximation provides a complete basis in terms of normal coordinates which can be used to diagonalize a general Hamiltonian. In the standard notation the harmonic basis is labeled by [59]

$$|v\rangle = |v_1 v_2 v_3\rangle, \tag{1}$$

where v_1 and v_3 correspond to the symmetrical and antisymmetrical stretching modes (A) and (B), respectively, while v_2 stands for

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